

Groundwater Contamination by Trace Level
Organics from a Rapid Infiltration Site

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GROUNDWATER CONTAMINATION BY TRACE LEVEL ORGANICS FROM A RAPID INFILTRATION SITE

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Abstract The trace organic removal efficiency for a rapid infiltration system is described. A broad spectrum monitoring of trace organics in the secondary sewage effluent applied to a rapid infiltration site is compared to a similar broad spectrum analysis of the groundwater beneath the site. Overall removal efficiency was about 92%. A chemical class breakdown of the organics yields removal efficiencies from 70 to 100%. The effects of groundwater dampening on concentration fluctuations was also treated over a 5-day period, showing very little difference over this time period.

INTRODUCTION

Land treatment offers a number of advantages including low initial cost, lower operating costs, potential for revenue to offset operating costs, and low energy requirements (Loehr *et al.*, 1979). Of the land treatment methods available, rapid infiltration is the most land intensive with infiltration rates from 30 to 120 m yr⁻¹ (100-400 ft yr⁻¹) (Sheaffer, 1979).

There are more than 360 land treatment sites in the United States with many more planned (Sheaffer, 1979). Yet, very little is known about the effectiveness of such sites to remove typical volatile refractory organic compounds or viruses from wastewater (Johnson, 1979). Of the normal measures of water quality, only nitrogen is typically a problem, but with proper application management rapid infiltration basins often achieve satisfactory reduction in total nitrogen (Sheaffer, 1979).

Prior to this research, the Muskegon County, MI irrigation site was the only land application site at which trace level organics removal had been studied. In that study it was found, out of the 59 gas chromatographable organics in the influent sewage, that only 19 were present after lagooning and eight were present in the final effluent after irrigation (Dunlap *et al.*, 1977). At least 11 compounds in the influent appear on the EPA "List of Dangerous Pollutants" and four of the eight compounds in the final effluent are toxic, including atrazine and trimethylisocyanurate. Even though known toxic pollutants appeared in the final effluent, their concentrations were greatly reduced. Also, there was probably minimal effect upon the associated groundwater because the whole system was underdrained by tiles at 2.1 to 3.3 m (7-11 ft) and the water was collected and pumped to a nearby creek which runs into Lake Michigan.

In contrast to the model Muskegon County irrigation site, most rapid infiltration sites allow their influent water to percolate down to the associated

groundwater aquifer. Similarly, most irrigation sites are not tile underlined and the applied wastewater either evaporates to the atmosphere or percolates down to the groundwater. Once an aquifer is polluted, decontamination may take from decades to centuries because of the absence or reduction of biodegradation, photolysis, oxidation, volatilization, and organic-related adsorption, all processes active in surface water decontamination.

Research reported here on the 23rd Avenue Project rapid infiltration site in Phoenix, AZ, helps assess the effectiveness of land application for the removal of trace level organics from wastewater. This 0.5 km² (120 acres) site was constructed in 1974. Its design was based in part upon engineering criteria developed at the Flushing Meadows Project, a small research site nearby (Bouwer, *et al.*, 1974). The 23rd Avenue Project consists of four parallel 0.04 km² (10 acres) infiltration basins and an 0.3 km² (80 acres) holding pond (Fig. 1). The system is designed to treat 13 mgd of secondary effluent by infiltration. The renovated water is supposed to be recovered by a large irrigation pump to prevent groundwater contamination and to provide water for agricultural reuse.

A further objective of this research was to establish the short- and long-term variation in the type and amount of individual compounds reaching the groundwater zone beneath a rapid infiltration site. To accomplish this objective two sampling trips of varying duration were made. Implications of these results for the overall effectiveness of rapid infiltration to remove trace level organics from wastewater and for the importance of sampling frequency are discussed.

Preliminary data concerning the site characteristics and the sewage were gathered in two previous trips. Soil column effluents (Flushing Meadows site) were examined using the methodology presented in this paper as a check on our analytical procedures and as baseline information for further data collection. A

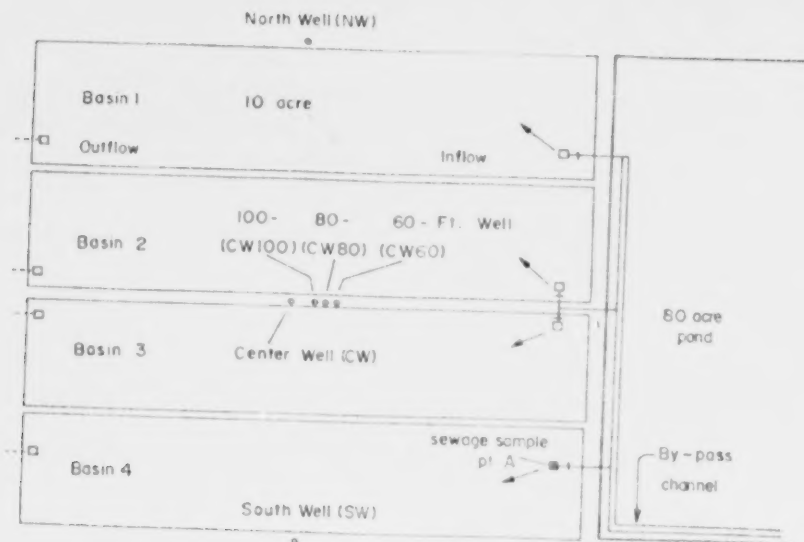


Fig. 1. Schematic of 23rd Avenue rapid infiltration project.

second trip (the first field testing of the 23rd Avenue site) consisted of site familiarization and data collection for an initial estimate of removal efficiencies. The second trip also served to refine the techniques and equipment used for the field experiments which followed.

EXPERIMENTAL

Sampling

Column sampling. Eight 2.75×0.15 m (9.0 $\times$ 0.5 ft) PVC columns associated with the nearby Flushing Meadows Project were sampled 14 April 1979. These columns have been shown to model BOD, COD, total nitrogen (T_N), and total phosphorus (T_P) removal found in the small Flushing Meadows Project rapid infiltration basins. The field basins were not sampled because they had been destroyed by flooding from the Salt River a few months earlier.

Each column was filled with 6 cm (2.4 in.) of pea gravel and then with 250 cm (98 in.) of loamy sand. Secondary sewage from the Phoenix treatment plant was pumped onto the head of each column. To obtain the necessary flow rate for the sampling apparatus, the effluents from four columns were combined. One group of four columns was "conditioned" by (1) applying sewage for 9 days, (2) allowing 5 days drying and, (3) applying sewage for 4 days just before sampling. Application of sewage to the other group of four "unconditioned" columns began at the same time sampling started. The raw secondary sewage being applied was also sampled.

Soil Cores. During the final trip, several soil cores were obtained at the 23rd Avenue site from Basin No. 2 (Fig. 1) with a 2.5 cm (1 in.) i.d. stainless-steel corer. Beginning 7 days after flooding, each day for 4 days, a 200 g sample of the top 10 cm (4 in.) of Basin No. 2 was collected and stored in a glass bottle with a Teflon-lined lid. On the ninth day after flooding, a pit was excavated in the center of Basin No. 2 and 200 g samples were taken at 2.5, 7.6, 15.2, 30.5, 61, 91, and 122 cm (1, 3, 6, 12, 24, 36, and 48 in.) depths.

One hundred grams of soil from each depth were extracted with 100 ml of 1:1 (v/v) hexane acetone on an Eberbach shaker for 24 h. The hexane acetone supernate

was decanted, centrifuged (2750 rpm, 1 h, 10°C) and the aqueous layer discarded. The hexane acetone supernate was then passed through a 10 ml Florisil column, and finally concentrated to 1 ml in a Kuderna-Danish concentrator. This workup is similar to the procedure used by Dunlap (1976). The percent moisture in the depth samples was determined by air drying at 105°C for 8 h.

Preliminary sampling at 23rd Avenue. On 24-27 January 1980, preliminary samples were obtained from the 23rd Avenue Project. Twenty-five liters of secondary sewage basin influent was obtained at Point A, Fig. 1. The 18.2 m (60 ft) center well (CW60) had in place a 0.9 m in length, 10 cm dia. (3 ft in length, 4 in. in dia.) Berkeley Model No. 4AM8 all stainless-steel (except the hard plastic impeller and insulation coated power cord) completely sealed submersible pump used for groundwater sampling, rated at 38 l min^{-1} . It has been suggested that most commercial electric pumps cannot be used to obtain groundwater samples for trace level organics analysis because trace level organics from the bearing, plastic components, etc. are continuously being released to the water. To test the effects of such a pump on the sampling procedure, two samples were taken at the same time, one using the installed submersible pump and one using an all glass and Teflon nitrogen-powered pump developed in our lab (Fig. 2) (Tomson *et al.*, 1980). The glass and Teflon pump was lowered down the CW60 well casing to a few feet below the submersible pump. During the 12 h required for sampling, the submersible pump discharged about $2.7 \times 10^4 \text{ l}$ of water through a hose to Basin No. 3. The 60 ml min^{-1} flow required for the XAD-2 column was obtained via a 0.64 cm (1/4 in.) steel tee screwed into the submersible pump riser pipe a few inches above the casing top. A variable speed peristaltic pump (Masterflex) located after each XAD-2 resin column was used to control the water flow rate through the columns.

Final 23rd Avenue sampling trip. A final extensive sampling trip to the Phoenix, AZ, 23rd Avenue Project was made 26 February-1 March 1980. One of the primary objectives of this trip was to determine the temporal variations in groundwater quality beneath a rapid infiltration site. Details of the sampling schedule are reported in Table 1. Although the Phoenix area had been flooded the previous week, it was not expected to have had any signifi-

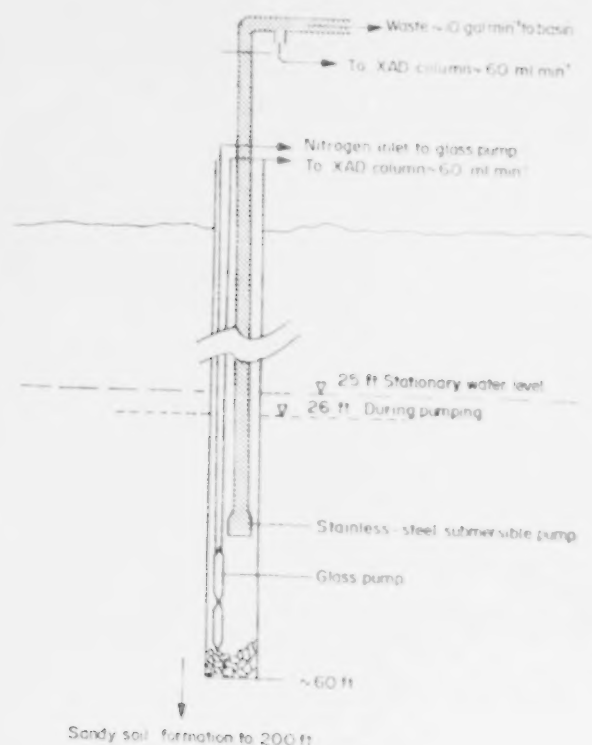


Fig. 2. Location of glass sampling pump with reference to the submersible pump.

cant effect upon the area groundwater. To confirm that the sewage and groundwater sampled were characteristic of the infiltration system, seven typically measured water quality parameters were measured for comparison: (1) conductivity, (2) pH, (3) DO, (4) T_p , (5) T_s , (6) temperature, and (7) water level. The sampling was carried out in the same manner as the first trip to the 23rd Avenue site.

Chemical adsorbent

Organic compounds were adsorbed and concentrated on Amberlite XAD-2 macroreticular resin (Rohm & Haas, Philadelphia, PA). This resin is a low-polarity, styrene-divinylbenzene copolymer with excellent surface characteristics for the adsorption of lipophilic contaminants (Junk *et al.*, 1974). The resin was purified by decanting the fines

Table 1. A list of the samples collected at the 23rd Ave site in Phoenix, AZ 26 February 1980 to 1 March 1980.

Date	Sample No.	Well	Volume (l)	Pump type*
26 Feb	100	CW 60 [‡]	21	S + M
26 Feb	101	CW 80	14	S + M
26 Feb	102	Sewage	19	M
27 Feb	103	CW 60	25	S + M
27 Feb	104	North	28	S + M
27 Feb	105	South	25	M
28 Feb	106	CW 60	25	S + M
28 Feb	107	CW 100	24	G
28 Feb	108	North	22	S + M
29 Feb	109	CW 60	20	S + M
29 Feb	110	CW 80	23	G
29 Feb	111	Sewage	14	M
29 Feb	112 [†]	Lab	22	M
1 March	113	CW 60	24	S + M
1 March	114	South	28	G

* M = Masterflex pump, S = submersible pump, G = glass pump.

[†] Typical drinking water of the Phoenix area.

[‡] CW 60, CW 80, CW 100 refer to 60, 80, and 100 ft center wells (Fig. 1).

from a slurry and by sequential solvent extractions with methanol, acetonitrile, and diethyl ether for 24 h each in a Soxhlet extractor. Amberlite XAD-4 and XAD-8 resins were also examined for comparative adsorption efficiencies. For a synthetic solution of 24 organic compounds typically found in contaminated water, XAD-2 proved to be equal to or better than the other resins in overall extraction efficiency. The possibility of humic acid interferences with XAD-2 recovery of trace level organics was similarly investigated. Using duplicate samples spiked with trace quantities of 14 refractory organic compounds, recovery efficiencies were compared to identical spiked samples to which various amounts of a synthetic humic acid preparation (Aldrich, Milwaukee, WI) had been added. There was no observable interference with compound recovery at humic acid concentrations of $1 \text{ ng} \cdot 10 \text{ mg l}^{-1}$.

Reagents. All solvents used for preparation and analysis were "distilled in glass" grade (Burdick & Jackson, Muskegon, MI) and each was checked by gas chromatography prior to use for the presence of interfering trace level organics. To obtain "organic-free" water, Rice University well water was initially passed through a mixed-bed resin column consisting of XAD-4, XAD-7, and XAD-8 resins and then finally through an XAD-2 resin column. Analysis of the purified water confirmed that it was acceptable for trace level organic measurements. Reagent-grade anhydrous sodium sulfate was stored in an oven at 250°C . Organic standards for sample verification, extraction tests, and recovery studies were obtained from a variety of sources (Aldrich, Milwaukee, WI; Pfaltz & Bauer Research Chemicals, Stanford, CT; Chem Service, Inc., West Chester, PA; Fisher Scientific, Houston, TX). The majority were reagent grade or better. Combination standards were prepared in chloroform and stored at -10°C prior to use. Combination standards consisted of a series of chemicals well within the limits of GC resolution for sample verification and quantification.

Sample collection and workup

Although analysis details of various individual samples differed, the following general scheme was used and only minor differences are noted. Sampling consisted of passing 10–50 L of groundwater or sewage through a $15 \times 0.9 \text{ cm}$ ($5.9 \times 0.35 \text{ in.}$) i.d. Teflon column filled with purified XAD-2 resin. After sample collection, these columns were stored on ice until laboratory workup. In the laboratory, the resin column was drained of the small amount of excess water. A 20 ml volume of diethyl ether was then added and allowed to penetrate into the resin for 10 min. The ether eluate was drained into a 125 ml separatory funnel. The extraction and elution was repeated with a second 20 ml volume of ether. An aqueous layer which formed in the separatory funnel was discarded. To dry the combined eluate, 15 g Na_2SO_4 was added to the separatory funnel.

After shaking for 2–3 min the ether extract was drained into a concentration vessel. The concentration vessel was a 50 ml round bottomed flask with the end of a 10 ml conical shaped graduated test tube sealed to the bottom. A small carbonadium bonding clip was added and the ether was distilled through a Vigreux column using a steam bath. When the level of the ether extract was 0.5 ml or less, the apparatus was removed from the steam and the outside of the concentration vessel was sprayed with acetone. The evaporation of acetone results in a condensation of the ether vapor which provided a systematic rinse of the inside walls of the vessel. The column was then adjusted to 1 ml with ether and the concentrate was transferred to Pierce Reacti-Vials[®] for storage. The concentrated extract was analyzed as soon as possible and stored at -10°C pending further use. An extra Teflon column was taken on each field trip and was returned without use. In each case it was extracted as above and served as a blank for that trip.

A gas chromatogram of each of the extract concentrates was obtained on a Tracor 560 chromatograph fitted with a 50 m fused silica Hewlett Packard SP2100 WCOT capillary column. The injection temperature was 250°C and helium flow rate one $\text{ml} \cdot \text{min}^{-1}$. Temperature program was 80°C for 4 min and $8^\circ\text{C} \cdot \text{min}^{-1}$ to a final temperature of 250°C . The chromatograms were recorded on a Spectra-Physics 4100 integrating computer. A portion of each sample was then spiked with Dinaphthalene and mass spectral analysis performed on a Finnigan 4000 MS using a matched GC capillary column. GC confirmation was performed by known addition or by retention time matching on as many compounds as could be obtained. In most cases quantification was based upon internal standards using the SP 4100 integrated peak areas. Final quantification of all compounds for which no pure standard could be obtained was by relative FID response. Many of the standards arrived too late to reliably quantify the stored samples and hence were quantified by relative FID response. For each compound, the same method of quantification was used for all reported samples and therefore all conclusions are based upon concentrations ratios.

RESULTS AND DISCUSSION

A summary of the refractory volatile organic (RVO) compounds found in this study is presented in Table 2. The "purity" index in Column 2 is a measure of how well a library mass spectrum and the corresponding sample spectrum match. From experience with groundwater and sewage samples similar to these, it has been found that the average purity index

Table 2. Refractory volatile organics ($\mu\text{g l}^{-1}$), 23rd Ave Project, Phoenix, AZ^a

Compound	Purity index	GC conf	Sewage			CW60 Groundwater			
			102	111	100	103	106	109	113
1. Trichloroethylene	947		0.032	0.038					
2. Toluene	958	x ^b	0.964	1.310	0.017	0.009	0.008	0.019	0.024
3. Tetrachloroethylene	979	x	0.251	0.050	0.029	0.021	0.034	0.065	0.074
4. 2,4-Dimethyl-3-hexanol	684		0.011	0.008	0.007	0.005	0.004	0.006	0.007
5. Chlorobenzene	764	x	0.015	0.008	P ^c	0.002	0.002	0.002	0.002
6. 1,3,5,7-Cyclooctatetraene	933				0.030	0.007	0.008	0.015	P
7. <i>p</i> -Xylene	968	x	2.140	4.050	0.049	0.010	0.040	0.011	0.019
8. <i>o</i> -Xylene	960	x	0.210	0.168					
9. Diethyldisulfide	979		0.015	0.036					
10. Propylbenzene	824	x	0.056	0.021					
11. <i>m</i> -Ethyltoluene	881	x	0.234	0.129					

Table 2. continued.

Compound	Purity index	GC conf.	Sewage		CW60		Groundwater		
			102	111	100	103	106	109	113
12. <i>o</i> -Ethyltoluene	924	x	0.105	0.049					
13. 1,3,5-Trimethylbenzene	908	x	0.132	0.047					
14. 1,2,3-Trimethylbenzene	945	x	0.128	0.085					
15. 1,2,4-Trimethylbenzene	913	x	0.332	0.129	P				
16. <i>m</i> -Dichlorobenzene	947	x	0.263	0.008	P				
17. <i>p</i> -Dichlorobenzene	943	x	0.617	0.355	0.042	0.022	0.043	0.072	0.069
18. <i>o</i> -Dichlorobenzene	945	x	0.986	0.210					
19. 1-Methyl-4-isopropyl-7-oxabicyclo-[2,2,1]-heptane	808		0.128	0.085					
20. 1-Chloro-2,3-dihydro-1H-indene	927				0.025	0.017	0.040	0.060	0.070
21. 1,1-Bicyclopentyl	910		0.006	0.080					
22. 2-Ethyl-1,4-dimethylbenzene	915		0.008	0.080					
23. 1-Methyl-2-isopropylbenzene	770	x	0.008	0.080					
24. 1-Methyl-4-isopropylbenzene	734	x	0.086	0.132					
25. Fenchone	706	x	0.075	0.056					
26. <i>m</i> - or <i>p</i> -Cresol	881	x	0.075	0.078					
27. 1,2,3,4-Tetrahydronaphthalene	773		1.490	1.980					
28. Camphor	582	x	0.164	0.008					
29. 1,6-Dichloro-1,5-cyclooctadiene	791				0.011				
30. 2,3-Dihydro-1H-inden-1-one	866		0.087	0.079					
31. 1-(4-Ethylphenyl)ethanone	716		0.006	0.026					
32. <i>p</i> -Isopropylphenol	491	x	0.061	0.028					
33. α -Terpineol	581	?	0.045	0.008					
34. 2-Methylnaphthalene	581	x	0.226	0.396					
35. 1-Methylnaphthalene	811	x	0.50	0.059					
36. 3,3-Dimethylhexane	850		IPs	IP	0.012	0.004	0.009	0.011	0.009
37. <i>p</i> - <i>t</i> -Butylphenol	748		0.125	IP					
38. <i>p</i> - <i>t</i> -Butylphenol	722		0.150		0.118	0.040	0.048	0.069	0.046
39. <i>m</i> - <i>t</i> -Butylphenol	849	x	0.189	0.116	P				
40. <i>p</i> - <i>t</i> -Butylphenol	738		0.819	0.907	0.069	0.035	0.090	0.097	0.074
41. 1H-Indole	662	x	0.009	0.086					
42. Skatole	901		0.030	0.031					
43. Undecane	773					0.004			
44. 3,5,24-Trimethyltetracontane	742		0.095	0.110					
45. Dimethylphthalate	585	x	0.023	0.015					
46. 1,2-Dihydro-2,2,4-trimethylquinoline	720				0.093	P	0.019	0.021	0.056
47. 2,6-Di- <i>t</i> -butyl- <i>p</i> -benzoquinone	760		0.022	0.037	0.005	P	P	P	P
48. <i>o</i> -Decylhydroxylamine	687		0.005	0.008					
49. 2,6-Di- <i>t</i> -butyl- <i>p</i> -cresol	887		0.267	0.250	0.056	0.200	0.071	0.096	0.079
50. <i>t</i> -Butyl-4-methoxyphenol	687		0.008	0.131					
51. α -Hydroxybenzoic acid	779		0.008	0.082					
52. 1,6-Dioxacyclododecane-7,12-dione	735				0.021		P	P	P
53. <i>o</i> -Phenylphenol	751		0.008	0.008					
54. Butoxymethylbenzene	760				P	0.005	0.007	0.008	0.005
55. Nonylbenzene	808		0.008	0.680					
56. Diethylphthalate	905	x	0.231	0.008	0.017	P	P	P	P
57. 2-Methylthio-benzothiazole	711	x	0.193	0.202	0.028	0.004	0.023	0.016	0.011
58. Benzophenone	804	x	0.233	0.285	0.045	0.016	0.014	0.014	0.009
59. 2-Propyl-1-heptanol	803				0.005	0.003	0.012	0.008	0.006
60. <i>p</i> -(1,1,3,3-Tetramethylbutyl)phenol	923	x	0.757	0.809	0.017	0.010	0.014	0.013	0.012
61. <i>p</i> -(2,2,3,3-Tetramethylbutyl)phenol	896		0.156		0.103	0.107	0.053	0.072	0.042
62. N-(3-Methylphenyl)acetamide	773		IP	IP	0.110	0.114	0.030	0.041	0.025
63. Hexadecane	703		0.052	0.057					
64. Hexatriacontane	852		0.035	0.036	0.130	0.271	0.095	0.028	0.090
65. Hexatriacontane	850		0.120	0.022	P	P	P	P	P
66. 4,6,8-Trimethyl-1-nonene	849					0.013			
67. Dibutylphthalate	957		0.248	0.260	0.316	0.729	0.274	0.314	0.239

* A blank indicates complete absence of the compound whereas a less than symbol (<) is used to indicate that the compound was detected in the GC and the MS traces, but at a concentration too close to background to quantify further; the associated number was the approximate detection limit for that run at that sensitivity in that region of the spectra.

† An "x" indicated that the compound identity was confirmed by GC retention time matching with a pure standard of that compound.

‡ P indicates compound was present, but at too low concentration to estimate.

§ IP indicates that the corresponding GC and GC/MS peak could not be reliably separated from background peaks.

and standard deviation of compounds subsequently confirmed by GC retention time matching has been about 830 ± 150 . Therefore, only compounds which have either confirmed by GC retention time matching ("x" in Column 3) or have a "purity" >680 , are reported. The compounds reported in Table 2 constitute 54% by number, of compounds identified, but from 75 to 85% of the RVO mass (estimated by area under the GC trace). In addition to the RVO's listed, 3-methylpentane, 2-isopropoxy-1-propanol, ethyl acetate, chloroform, 2,4,6-trimethyl-1,3,5-trioxane, and 1,1,1-trichloroethane with purity indexes 929, 793, 916, 993, 861, and 959, respectively, were identified by mass spectral analysis to be under the solvent peak, prior to trichloroethylene.

The compounds in Table 2 are listed in the approximate order that they elute from the capillary GC column with a few exceptions of isomers which have been grouped together. We have found that the Mass Spectral Search System (MSSS) used in this study to assist in compound identification often fails to correctly differentiate between closely related isomers such as the various trialkylbenzenes, tetraalkylbenzenes, dichlorobenzenes, methyl-naphthalenes, and different high molecular weight alkanes, but for "purity" >680 rarely is the compound class or overall carbon number in error. If the compound was also confirmed by GC retention time matching, there is little uncertainty in its specific identity. For example, we are certain of the class and identity of the six alkylbenzenes Nos. 10-15, but for compounds Nos. 37-40 we are only certain that they form alkylphenols with the exception of No. 39 which has been confirmed to be *m*-butylphenol. An overall estimate of the uncertainty in the concentrations was made by various repetitive injections, extractions, etc. and probably is within a factor of ± 1.0 to ± 2.0 of the value for compounds $<0.1 \mu\text{g l}^{-1}$ to about ± 0.2 to ± 0.5 of the value reported for concentrations $>0.1 \mu\text{g l}^{-1}$.

For the analytical reasons discussed above and

because compounds of one chemical class often have similar biological, physical, and chemical properties, the sum of compound concentration by chemical class are listed in Table 3. The overall weighted average RVO removal was 92%. When all compounds were considered, regardless of "purity" index, the removal was from 16,578 to $2,245 \mu\text{g l}^{-1}$, or 86.4%. The difference was not clearly attributable to any given class. From Table 3 it can be seen that most classes of compounds are removed from 90 to 100%. Noted exceptions are chloroalkanes, alkylphenols, alkanes, phthalates, and amides. The phthalate datum in Table 3 may be in error as previous analyses of other sites and other data indicates phthalate removal generally ranges from 70 to 80%. If the phthalate datum is omitted from Table 3, the ARVO_{90} only increases from 92 to 94%.

An additional objective of this research was to determine the concentration variation with time for groundwater samples. It can be seen from Table 2 that if a compound appears in one CW60 sample at a measurable concentration, it generally appears in all five samples, but some of the compounds such as undecane (No. 43) can barely be differentiated from noise. To further test this idea, a two-factor analysis of variance (ANOVA) without replication was performed on the 29 compounds marked "x" in Table 2 (Zar, 1974). For all of these compounds, the concentration in the CW60 groundwater was measurable three or more days. The data were log-transformed before analysis in order for the variances of the five CW60 to be similar in size (Zar, 1974). The hypothesis that the 5 CW60 samples are the same was accepted at the 0.98 level. Therefore, due to visual similarity of the chromatograms (Fig. 3), to the general qualitative appearance of a compound in all CW60 samples, and to the ANOVA statistical test, it is concluded that there is little variation with time in the qualitative or quantitative nature of the RVO compounds beneath such a rapid infiltration system.

Table 3. Refractory volatile organics ($\mu\text{g l}^{-1}$) by class, 23rd Ave. Project, Phoenix, AZ

Class (typical example)	Purity >680		ARVO ₉₀
	Average sewage	Average CW60	
1. Chloroalkanes (tetrachloroethylene)	0.186	0.056	70
2. Chloroaromatics (<i>p</i> -dichlorobenzene)	0.922	0.055	94
3a. Alkylbenzenes (<i>o</i> -xylene)	5.943	0.123	98
3b. Alkylphenols (<i>p</i> -isopropylphenol)	1.624	0.241	85
4. Alkyl-naphthalenes (2-methylnaphthalene)	2.101	0.0	100
5a. Alkanes (hexatriacontane)	0.671	0.193	71
5b. Alcohols (2,4-dimethyl-3-hexanol)	0.132	0.006	95
5c. Ketones (2,6-di- <i>t</i> -butyl- <i>p</i> -benzoquinone)	0.197	0.004	98
6. Phthalates (diethylphthalate)	0.385	0.379	2
7. Indoles, Indenes (1H-indole)	1.736	0.071	96
8. Amides (N-[3-methylphenyl]acetamide)	0.212	0.055	74
9. Alkoxyaromatics (butoxymethylbenzene)	0.107	0.010	91
Total	14.216	1.193	
$\text{ARVO}_{90} = \left(\frac{\sum \text{Sew} - \sum \text{CW60}}{\sum \text{Sew}} \right) \times 100\%$			92

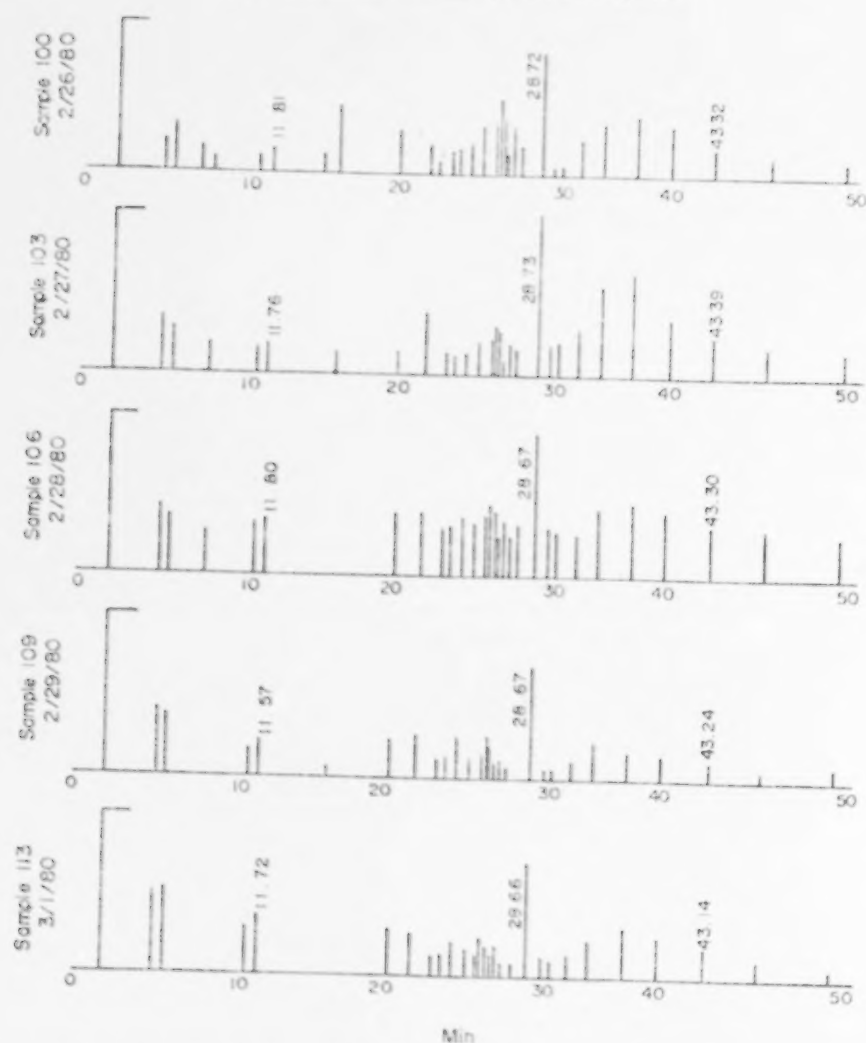


Fig. 3. Graphic summary of major capillary GC peak positions and height found in the Phoenix CW60 well on 5 successive days (see Table 2 for analytical results).

Three major mechanisms, adsorption, volatilization, and biodegradation are probably responsible for compound removal (Tinsley, 1979). Since the sewage in this study is actually the effluent from an activated sludge plant located about a mile away, those compounds readily biodegraded probably would not appear in the sewage sample. Alexander recently reported that biodegradation at trace levels, i.e. below 1 ppm, may be orders of magnitude slower than expected from Monod kinetics (Boethling & Alexander, 1979). Also, it was shown in experiments on 2,3-dimethylnaphthalene (2,3-DMN) conducted in the authors' laboratory, that in the presence or absence of a high BOD, sewage bacteria reduce 1.3 mg l^{-1} 2,3-DMN to about $40 \text{ } \mu\text{g l}^{-1}$ in 1 day and then stop further uptake for several days (Tomson *et al.*, unpub-

lished results). Since the highest concentration of any organic analyzed in the sewage samples was *p*-xylene at $405 \text{ } \mu\text{g l}^{-1}$, the importance of biodegradation in this system may be minimal.

The relative importance of adsorption and volatilization can only be semi-quantitatively estimated. If adsorption follows a Freundlich isotherm with unit exponent, then the relative velocity of the water and the pollutant, v/v_{pol} , can be related to the soil/water partition coefficient, K_p :

$$v/v_{pol} = 1 + \frac{\rho_b}{n} K_p$$

where ρ_b represents bulk density ($\sim 2 \text{ g cm}^{-3}$) and n represents porosity (~ 0.3) (Freeze & Cherry, 1979). K_p can be taken as proportional to the fraction

organic carbon (OC) and the octanol/water partition coefficient, K_{ow} (Karickhoff, 1980):

$$Kp = (OC)(0.63)K_{ow}$$

Assuming an OC of 3%:

$$r/r_{pot} \approx 1 + 0.13 K_{ow}$$

Thus, any pollutant with a $K_{ow} \geq 270$ would be expected to move on the average ≤ 2.5 cm (1 in.) when as much as 91 cm (36 in.) of sewage is applied to a basin. It should be noted that since r refers to water velocity and $n \approx 0.3$, the actual distance of travel would be ~ 7.6 cm (3 in.) on the average. Since most compounds in Table 2 have $K_{ow} \gg 175$, it is expected that adsorption will be an important mechanism toward preventing groundwater contamination. Also, adsorption will cause the soil to act as a time release "buffer" to reduce any fluctuations in concentration in the groundwater due to fluctuations of concentration in the sewage. Dibutylphthalate, No. 67, may be an exception because $K_{ow} \approx 10^5$ which would correspond to a relative velocity of 2×10^4 and a highly damped concentration in the CW60 samples. Thus, the CW60 No. 103 sample concentration may be in error.

Evaporation rates from the applied sewage and from the soil are probably high for most of the compounds in Table 2. By the Knudsen equation the evaporation rate (half-life, t_1 [sec]) from water can be related to Henry's law constant, H (dyne cm g⁻¹), and the water depth, d (cm):

$$t_1 = \frac{0.693 d}{\beta H}$$

where β is a correction constant (2.5×10^{-5}) and $f = (M/2\pi RT)^{1/2}$ with M as molecular wt (Tinsley, 1979). The half-lives estimated from this equation range from approx. 10 min to 3 h for an average sewage depth of 30.5 cm (1 ft). In practice, d is probably less than 1 ft, but the applied sewage is not stirred; hence, these effects should compensate. Once the sewage has infiltrated and the trace organic pollutants adsorbed, evaporation from the basin soil will commence. Little data is available on evaporation rates from soil. The work of Spencer & Clith (1972) on lindane, with vapor pressure $P_v \sim 1.28 \times 10^{-4}$ Torr, can be used to establish a lower limit on evaporation rate for most compounds in Table 2. For soil of 100% relative humidity and 30°C from their data, t_1 for evaporation can be estimated at 6 h. Since the drying cycle is 21 days, one would estimate 99+% removal in about 2½ days for most of the classes of compounds listed in Table 3. Since much higher concentrations are found in the groundwater than would be predicted based upon either volatilization or adsorption there must be other unidentified mechanisms of transport operative.

SUMMARY

In summary, data has been presented which shows

1. Rapid infiltration basins are not totally (100%) efficient with respect to RVO removal.

2. The "dampening" effects of groundwater on organic contaminants results in very little daily concentration variation over a five day period, and

3. Classes of organic compounds exhibit different removal efficiencies ranging from 70 to 100%.

It is suggested for further work that concentration variations over a longer time frame be tested which would give a better indication of the ability of soil to dampen concentration fluctuations. Also, more bench and field studies are needed to test the apparent differences among removal efficiencies for various classes of compounds.

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